Accelerated Molecular Dynamics at the Solid-liquid Interface

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A long-standing problem in the atomistic simulation of materials is the fact that direct molecular dynamics (MD) techniques are limited to time scales of roughly one microsecond or less. Although computer speeds continue to increase, this limitation is not expected to change qualitatively in the near future. Parallel architectures can be used to increase the size scale of MD, but have little impact on the accessible time scale. For systems in which the long-time behavior can be characterized by infrequent events (typically thermally activated events) between well-defined states of the system, rate-based approaches can be powerful for overcoming this problem. In particular, accelerated molecular dynamics (AMD) methods developed over the last 10 years at LANL can often be used to access these longer time scales in an accurate, dynamical way. In the AMD approach, the core concept is to let the trajectory itself find an appropriate way to escape from each state, but in some way induce it to discover this escape path more quickly than it would under normal circumstances. In this approach, there is no need to guess at, or search for, all possible escape paths from each state, as in kinetic Monte Carlo (KMC) approaches. A discussion of both AMD and KMC methods can be found in [1].

There are many systems, however, that do not neatly fulfill the requirements for easy application of the AMD methods. A general class that is problematic is when the infrequent-event system is coupled with a complex and dynamic environment. The combined system makes much more rapid transitions, and direct application of AMD is pointless, since there is no computational gain. A specific example of this type of system is a solid surface in contact with a liquid. We might be interested in following the evolution of the surface morphology during electrochemical deposition or etching, or discovering the relevant steps of a surface-catalytic reaction or a corrosive process. As a step towards learning how to extend the AMD methods for treating this class of complex coupled systems, we have begun studying whether we can develop an AMD procedure that is valid for adatom diffusion at a model solid-liquid interface. This work also represents an important step in the development, for an ongoing Scientific Discovery through Advanced Computing (SciDAC) project, of a multiscale simulation capability for stress-corrosion cracking.

As hinted above, AMD methods rely on a large separation of time scales between vibrations of atoms within a state and escape from the state. However, this separation does not hold in liquids where vibration and diffusion occur on similar time scales (on the order of a picosecond). A naive application of the AMD methods would thus be overwhelmed by the incessant change of state of the liquid, and thus could not provide acceleration of the dynamics of the solid atoms, which are really the quantity of interest here. The problem at hand thus amounts to defining the concept of a superstate so that the separation of time scales between intra- and intersuperstate dynamics is restored, and then applying AMD methods at the superstate level.

A simple strategy to reach this goal is to define superstates based on the configuration of the slow degrees of freedom (DOF) in the system, i.e., every state in which the slow DOF are in the same configuration belong to the same superstate, notwithstanding the state of the fast DOF. If the typical time scale over which the fast DOF evolve is much faster than that of the slow DOF, the validity of the AMD methods should be assured and their efficiency restored.

For typical solid-liquid interfaces—for example, a metal in contact with a liquid like water at room temperature—this segregation of DOF into fast and slow subsets should be easy to define: coordinates of the liquid atoms form the fast subset while coordinates of the solid atoms form the slow subset, while transitions in such a liquid will occur thousands of times faster than rearrangements of the solid atoms.

To test that this definition is proper, we carried out superstate parallel-replica dynamics [2] simulations of the diffusion of an adatom on a silver (100) surface (modeled using the Embedded Atom Method [3]) in contact with a film of a prototypical fluid (modeled using a Lennard-Jones potential). The distribution of 500 adatom hopping times at 600 K is shown in Fig. 1 for a direct simulation using conventional molecular dynamics and for a superstate parallel replica simulation on eight processors. The results clearly show that transition statistics are equivalent for the two approaches, implying that our superstate definition restores the time-scale separation essential for the validity of the AMD methods. In this case the parallel replica simulation was quite efficient, with a parallel efficiency of around 0.8 despite the presence of very fast transitions in the liquid.

Note that the agreement is not due to a negligible effect of the liquid on the adatom dynamics. Indeed, as shown in Fig. 2, the transition rate of the adatom on the wet surface is around 1.6 times slower than on the dry surface at 600 K, increasing to a factor of 3.5 at 500 K. The rate corrections due to the liquid are thus significant and have a nontrivial temperature dependence. This further highlights the need to develop tools to study the peculiarities of the dynamics of solid-liquid interfaces.

In conclusion, we have demonstrated the possibility of adapting the AMD methods to systems in contact with fast-evolving complex environments. This ongoing work could help researchers tackle a wide range of technologically relevant problems like corrosion, liquid-metal embrittlement, or crystal growth and etching, by allowing these problems to be affordably studied at the atomic scale. While these results are encouraging, certain challenges remain, such as correctly treating the dynamics
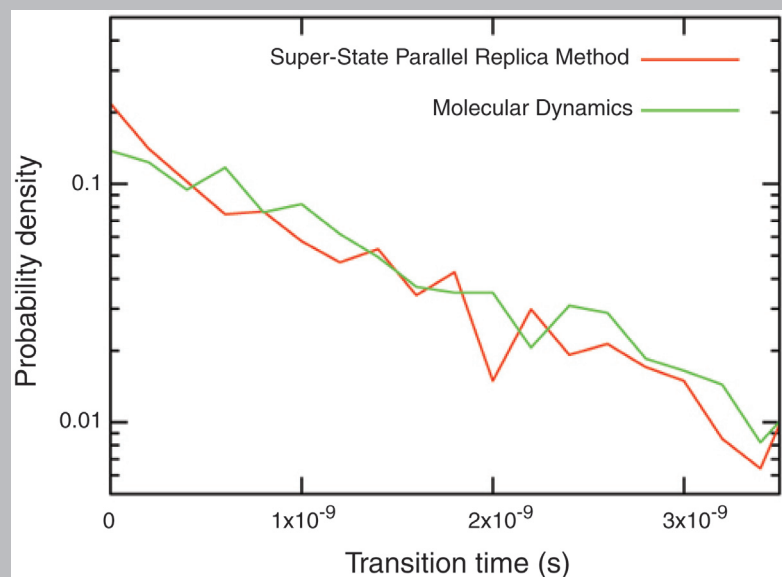
Fig. 2. Temperature dependence of the hopping rate for an adatom at a dry interface and at a wet interface.

Fig. 1. Distribution of hopping times for an adatom at a solid-liquid interface at 600 K.

of dissolved solid atoms and generalizing our superstate definition to include lower temperature cases where the dynamics of the liquid in the solvation layer is not necessarily fast compared with the dynamics of the solid.

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